Supporting Information

Polycyclic aromatic hydrocarbons in surface sediments of the mid-Adriatic and along Croatia coast: levels distributions and sources

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Additional information concerning analysis

Sediment-particles grain size and organic matter determinations were done by Institute of Oceanography and Fisheries, IOF, Šetalište I. Meštrovića 63. 21000 Split; Croatia.

PAH analyses were done in the Laboratory of Organic Contaminants Biogeochemistry at IFREMER, Nantes, France.

PAH summed concentrations account are: ΣPAH_{16} sum of: phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene + triphenylene, benzo[*bj*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[1.2.3-*cd*]pyrene, dibenz[*ah*]anthracene, benzo[*ghi*]perylene and coronene; **ΣC-PAH sum of**: C1, C2, C3-alkyl-phenanthrenes / anthracenes; C1, C2-alkyl-fluoranthenes / pyrenes; C1,C2,C3-alkyl-chrysenes; C1-alkyl-benzofluoranthenes (note that triphenylene is unresolved from chrysene and that benzo[*b*]fluoranthene is counted as unresolved from benzo[*j*]fluoranthene).

Table S-1. List of all sampling stations. site description. sampling depth. geographic coordinates and sampling periods.

Area	Station	Site description	Depth (m)	Latitude (DD) N	Longitude (DD) E	Sampling 2013
TRANSECT	**TS1**	Horizontally aligned with Island of Hvar	78	43.20000	16.31666	Feb. Aug.
	TS2	Horizontally aligned with Island of Vis	105	43.00000	16.33330	Feb. Aug.
	TS3	Horizontally aligned to Susac. small island	175	42.60000	16.26833	Feb. Aug.
	TS4	Horizontally aligned to Palagruza - lighthouse on a small rocky island	102	42.36660	16.22000	Feb. Aug.
	TS5	20 nautic miles distanced from "Monte Garagano"- Italian coast	116	42.13330	16.16660	Feb.
COAST	**CS1**	Near Island of Pag- town of Pag/	49	44.49005	15.01010	Mar.
	CS2	Novigrad Sea near Starigrad	49	44.28272	15.41285	Mar.
	CS3	Town of Zadar. western coast	33	44.11375	15.21542	Mar.
	CS4	Town of Zadar outer port	34	44.12576	15.21077	Feb.
	CS5	Between Zadar and Biograd. near to the new port of Zadar: "Gazenica"	61	44.02318	15.28622	Mar.
	CS6	Sibenik external near Island of Prvic	52	43.70396	15.80645	Mar.
	CS7	Sibenik external near Island of Zlarin	25	43.65000	15.86183	Mar.
	CS8	"Split gates" near Island of Brac	52	43.42666	16.39833	Feb.
	CS9	Split. West coast. Split touristic harbour	38	43.48643	16.44183	Feb.
	CS10	Town of Omis. near former factory for ferrum and chromium production	37	43.38127	16.90387	Feb.
	CS11	Entrance in the port of Ploce. external station	21	43.02608	17.41188	Mar.
	CS12	Dubrovnik external	110	42.63339	18.02187	Mar.
KASTELA BAY	**KB1**	Central station	38	43.51833	16.38166	Feb. Aug. Oct.
	KB2	Near the former plant for plastics production	30	43.53641	16.40658	Feb. Aug.
	KB3	Industrial port "Northern port of Split"	18	43.53000	16.45333	Feb. Aug. Oct.
	KB4	Near town of Trogir. western part of the Bay	22	43.51766	16.34633	Feb. Aug. Oct.
ŠIBENIK BAY	**SB1**	Marina-front	27	43.71939	15.89540	Feb. Aug. Oct.
	SB2	Port of Sibenik-front	17	43.72787	15.89468	Feb. Aug. Oct.
	SB3	Sibenik center. fisheries port	16	43.73498	15.88711	Feb. Aug. Oct.r
	SB4	Former ferroalloy factory-front	38	43.74136	15.88195	Feb. Aug. Oct.
	SB5	Sibenik bay. middle of the Bay	35	43.73730	15.88183	Feb. Aug. Oct.
	SB6	Marina-inner	14	43.72570	15.89972	Oct.
	SB7	Port of Sibenik-inner	17	43.72675	15.89471	Oct.
	SB8	Port of ferroalloy factory-inner	31	43.74350	15.88080	Oct.

Table S-2. Grain size distribution (weight %), organic matter content (weight %) and descriptive statistical parameters calculated for granulometry**.**

Area	Station	Month of 2013	Station Code	Gravel %	Sand %	Silt %	Clay %	OM %	Sorting So	Skewness Sk	Kurtosis Kg	Mean size Mz (μm)	Median Md (μm)
TRANSECT AREA	**TS1**	Feb	TS11	13.2	78.7	7.6	0.8	2.1	2.3	0.6	3.4	119.6	155.7
	TS2	Feb	TS21	1.7	83.7	5.4	9.2	2.6	2.4	0.3	3.5	160.3	167.4
	TS3	Feb	TS31	0.0	4.0	59.2	36.8	6.0	3.0	0.8	0.8	9.8	35.7
	TS4	Feb	TS41	3.9	87.9	3.3	4.9	1.7	2.1	0.4	2.0	472.5	541.0
	TS5	Feb	TS51	0.3	2.1	53.5	44.1	4.8	2.5	0.2	0.9	4.6	5.2
	TS1	Aug	TS12	0.8	81.1	6.2	11.9	1.6	2.3	0.5	3.3	130.9	154.6
	TS2	Aug	TS22	1.0	70.9	8.0	20.0	2.6	3.3	0.8	2.0	40.2	147.9
	TS3	Aug	TS32	0.1	3.7	68.1	28.1	4.7	2.9	0.9	0.9	10.6	39.0
	TS4	Aug	TS42	2.0	92.6	2.2	3.2	1.1	1.3	0.4	2.4	573.2	643.9
COASTAL AREA	**CS1**	Mar	CS1	0.0	1.6	46.1	52.3	2.0	2.9	0.3	0.7	2.3	3.5
	CS2	Mar	CS2	4.1	57.7	18.2	19.9	3.6	4.4	0.5	1.0	45.6	131.3
	CS3	Mar	CS3	3.6	21.8	51.7	22.9	4.2	4.1	0.3	1.7	16.4	34.8
	CS4	Feb	CS4	1.4	25.5	51.7	21.4	2.0	3.7	0.3	1.5	21.8	37.5
	CS5	Mar	CS5	4.1	41.5	22.8	31.6	1.4	4.7	0.3	0.8	20.7	41.4
	CS6	Mar	CS6	0.8	84.9	3.3	11.0	3.3	2.2	0.5	3.6	210.5	221.9
	CS7	Mar	CS7	4.2	76.1	4.5	15.1	4.4	1.3	0.1	0.5	2.3	2.6
	CS8	Mar	CS8	0.8	9.1	53.2	36.8	5.8	3.8	0.6	2.1	158.0	399.1
	CS9	Feb	CS9	2.6	0.6	67.7	29.2	4.6	3.0	0.7	0.9	7.7	22.3
	CS10	Feb	CS10	2.2	15.7	57.7	24.5	3.2	3.0	0.1	1.4	13.6	16.6
	CS11	Mar	CS11	4.7	2.6	46.8	45.9	3.7	3.8	0.1	1.0	3.4	5.8
	CS12	Mar	CS12	0.2	10.7	54.2	34.9	2.1	2.9	0.2	1.1	5.7	7.1
KAŠTELA BAY	**KB1**	Feb	KB11	0.7	2.6	50.9	45.8	2.3	2.7	0.1	0.8	4.5	4.4
	KB2	Feb	KB21	0.1	5.8	47.8	46.4	6.3	3.2	0.1	0.8	4.3	4.7
	KB3	Feb	KB31	5.6	40.2	33.8	20.4	4.2	4.2	0.2	1.0	43.1	59.8
	KB4	Feb	KB41	13.0	78.8	3.3	4.9	2.6	2.2	0.4	2.1	746.2	864.3
	KB1	Aug	KB12	1.3	4.7	51.2	42.8	3.3	3.2	0.0	0.9	5.5	5.0
	KB2	Aug	KB22	2.0	5.4	61.6	31.0	6.1	3.5	0.6	1.1	11.6	38.5
	KB3	Aug	KB32	0.4	11.1	61.8	26.6	4.4	3.1	0.3	1.2	11.5	18.7
	KB4	Aug	KB42	13.2	54.4	11.8	20.6	3.1	4.8	0.4	0.9	84.1	264.0
	KB1	Oct	KB13	0.5	1.1	48.2	50.2	3.5	2.7	0.1	1.1	4.0	3.9
	KB3	Oct	KB33	2.8	4.9	51.4	40.9	4.8	3.1	0.0	1.3	5.2	5.2
	KB4	Oct	KB43	21.4	48.1	13.5	17.1	2.9	4.8	0.5	0.9	175.5	529.8
ŠIBENIK BAY	**SB1**	Feb	SB11	1.7	5.2	51.3	41.8	10.7	3.4	0.2	1.0	4.3	6.7
	SB2	Feb	SB21	2.1	5.1	61.0	31.8	9.9	3.3	0.3	1.2	5.8	10.2
	SB3	Feb	SB31	14.6	79.9	2.2	3.3	3.5	1.9	0.0	1.7	699.0	669.1
	SB4	Feb	SB41	19.9	8.6	48.4	23.1	13.9	5.5	0.0	1.3	50.4	40.9
	SB5	Mar	SB51	0.7	4.1	68.4	26.9	8.8	2.6	0.0	1.5	4.3	3.9
	SB1	Aug	SB12	4.9	11.0	54.2	29.9	7.7	3.8	0.4	1.2	10.4	30.2
	SB2	Aug	SB22	0.8	5.0	52.7	41.5	7.0	2.9	0.0	1.0	5.3	5.1
	SB3	Aug	SB32	16.8	70.2	5.2	7.8	7.8	2.8	0.4	2.1	602.6	706.9
	SB4	Aug	SB42	4.3	6.1	75.3	14.2	10.3	2.5	0.6	27.6	33.2	57.1
	SB5	Aug	SB52	0.7	2.4	64.1	32.8	7.6	2.9	0.7	0.9	9.2	23.2
	SB1	Oct	SB13	1.9	31.8	26.6	39.7	9.7	4.5	0.0	0.7	10.8	11.5
	SB2	Oct	SB23	0.7	7.2	36.9	55.2	4.5	3.5	0.0	0.8	2.6	2.6
	SB3	Oct	SB33	35.6	39.2	10.4	14.9	8.5	4.8	0.5	1.0	317.8	995.3
	SB4	Oct	SB43	23.4	29.6	27.1	19.9	4.3	5.0	0.1	0.7	89.8	103.8
	SB6	Oct	SB6	0.8	47.9	35.8	15.5	9.5	3.0	0.4	2.2	40.7	62.0
	SB7	Oct	SB7	49.0	33.7	3.1	14.2	6.6	5.0	0.6	1.7	434.8	1896.2
	SB8	Oct	SB8	18.1	32.5	34.0	15.4	12.0	4.5	0.1	1.1	106.0	100.5

Table S-3: List of determined parent PAH. alkyl substituted PAH and sulphur heterocyclic PAH with abbreviations. quantification molecular weight ion. and internal standards used as references for quantitation.

Compound name	Abbreviation	Quantification ion (m/z)	Quantification standard
Phenanthrene	Phen	178	Fluorene-d_{10}
Anthracene	Anth	178	Fluorene-d_{10}
C1-phenanthrenes/anthracenes*	C1-P	192	Fluorene-d_{10}
C2-phenanthrenes/anthracenes**	C2- P	206	Fluorene-d_{10}
C3-phenanthrenes/anthracenes	C3- P	220	Fluorene-d_{10}
Fluoranthene	Fl	202	Pyrene-d_{10}
Pyrene	Py	202	Pyrene-d_{10}
C1-pyrenes/fluoranthenes	C1-Py	216	Pyrene-d_{10}
C2-pyrenes/fluoranthenes	C2- Py	230	Pyrene-d_{10}
Benz[*a*]anthracene	B*a*Anth	228	Benz[*a*]anthracene-d_{12}
Chrysene	ChrTri	228	Benz[*a*]anthracene-d_{12}
Triphenylene		228	Benz[*a*]anthracene-d_{12}
C1-chrysenes	C1-CHR	242	Benz[*a*]anthracene-d_{12}
C2-chrysenes	C2-CHR	256	Benz[*a*]anthracene-d_{12}
C3-chrysenes	C3-CHR	270	Benz[*a*]anthracene-d_{12}
Benzo[*b*]fluoranthene	B*bj*Fl	252	Benz[*a*]anthracene-d_{12}
Benzo[*j*]fluoranthene		250	Benz[*a*]anthracene-d_{12}
Benzo[*k*]fluoranthene	B*k*Fl	252	Benz[*a*]anthracene-d_{12}
C1- Benzofluoranthenes	C1-BFls	266	Benz[*a*]anthracene-d_{12}
Benzo[*e*]pyrene	B*e*Py	252	Benz[*a*]anthracene-d_{12}
Benzo[*a*]pyrene	B*a*Py	252	Benz[*a*]anthracene-d_{12}
Perylene	Per	252	Benz[*a*]anthracene-d_{12}
Indeno[1.2.3-*cd*]pyrene	IPy	276	Benz[*a*]anthracene-d_{12}
Dibenz[*ah*]anthracene	DBA	278	Benz[*a*]anthracene-d_{12}
Benzo[*ghi*]perylene	BghiPe	276	Benz[*a*]anthracene-d_{12}
Dibenzothiophene	DBT	184	Fluorene-d_{10}
C1-dibenzothiophenes	C1-DBT	198	Fluorene-d_{10}
C2-dibenzothiophenes	C2-DBT	212	Fluorene-d_{10}
C3-dibenzothiophenes	C3-DBT	226	Fluorene-d_{10}
Benzo[b]naphtho[2.1-*d*]thiophene		234	Pyrene-d_{10}
Benzo[b]naphtho[1.2-*d*]thiophene	BNTs	234	Pyrene-d_{10}
Benzo[b]naphtho[2.3-*d*]thiophene		234	Pyrene-d_{10}
C1-benzonaphthothiophene	C1-BNTs	248	Pyrene-d_{10}

*C1-phenanthrenes/anthracenes: summed 3-Methylphenanthrene. 2-Methylphenanthrene 2-Methylanthracene. 9-Methyl phenanthrene and 1-Methylphenanthrene

**C2-phenanthrenes/anthracenes: 3-ethylphenanthrene ; 2 and 9-ethylphenanthrenes and 3.6-dimethylphenanthrene ; 2.6-dimethylphenanthrene ; 2.7-dimethylphenanthrene ; 1.3-. 2.10-. 3.9-. and 3.10-dimethylphenanthrenes; 1.6- and 2.9- dimethylphenanthrenes; 1.7-dimethylphenanthrene; 2.3-dimethylphenanthrene; 1.9- and 4.9-dimethylphenanthrenes; 1.8-dimethylphenanthrene.
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Table S-4. Summed concentration of PAHs (μg.kg^{-1} dry weight) at all sampling stations (average concentrations for the transect and Kaštela and Šibenik bays) in the surface sediments of the offshore mid-Adriatic area and along the Croatian coast.

	STATION	∑PAH μg kg^{-1}	∑C-PAH μg kg^{-1}	∑S-PAH μg kg^{-1}	∑CS-PAH μg kg^{-1}
TRANSECT	TS1	13.6	6.11	0.658	1.61
	TS2	18.6	12.5	0.690	2.23
	TS3	58.160	49.9	2.40	4.80
	TS4	8.96	3.64	0.372	0.439
	TS5	146	135	4.20	13.3
COASTAL ZONE	CS1	85.9	31.1	3.03	4.46
	CS2	288	313	31.0	158
	CS3	1747	832	27.5	92.7
	CS4	370	226	17.4	44.0
	CS5	153	46.9	6.71	7.77
	CS6	234	110	13.8	18.3
	CS7	106	43.6	4.43	7.19
	CS8	141	48.6	4.13	6.29
	CS9	125	57.3	5.63	9.27
	CS10	1279	822	65.0	153.2
	CS11	159	118	6.31	19.8
	CS12	503	255	14.9	22.2
KAŠTELA BAY	KB1	362	215	17.0	47.1
	KB2	261	161	16.2	53.5
	KB3	838	803	57.6	279
	KB4	134	73.4	11.0	33.8
ŠIBENIK BAY	SB1	6485	2906	275	223
	SB2	6512	2689	265	246
	SB3	9578	3200	291	187
	SB4	16024	5076	313	452
	SB5	5320	1290	248	147
	SB6	16586	5253	266	588
	SB7	5617	2858	309	383
	SB8	18806	5770	371	977

Σ PAH: Sum of unsubstituted compounds phenanthrene. anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene + triphenylene, benzo[*b*]fluoranthene+ benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a*,*h*]anthracene, benzo[*ghi*]perylene,

Σ C-PAH: Sum of alkyl-phenanthrenes / anthracenes, alkyl-fluoranthenes / pyrenes, alkyl-chrysenes, alkyl-benzofluoranthene.

Σ S-PAH: Sum of unsubstituted dibenzothiophene and three isomers of benzonaphthothiophenes.

Σ CS-PAH: Sum of alkyl- substituted dibenzothiophnes and benzonaphthothiophenes.

Table S-5. Alkyl/Parent PAH ratio arranged from the lowest to the highest with relative source contributions apportionment (weight % of two pyrogenic and one pathogenic source) calculated by alternative least square - ALS method (Pirouette /Infometrix). Source identifications: Pyro FLPY for Pyrogenic 1 (with high fluoranthene and pyrene contributions). Pyro B(BJ)FL for Pyrogenic 2 (with high benzo(bj)fluoranthene contribution) and Petro for petrogenic.

STATION	*ALKYL/PARENT ratio*	*PYRO FLPY (%)*	*PYRO (BJ)FL (%)*	*PETRO (%)*
SB51	0.23	0.9	94.3	4.8
SB21	0.27	1.9	85.9	12.2
SB32	0.28	33.2	66.8	0.0
SB52	0.28	5.0	83.6	11.4
SB31	0.28	22.8	73.9	3.3
SB41	0.30	4.8	84.9	10.3
SB42	0.31	4.2	85.4	10.4
SB83	0.31	14.5	71.9	13.7
CS5	0.32	32.8	41.7	25.6
SB63	0.32	1.1	84.4	14.5
CS82	0.35	0.0	85.0	15.0
CS81	0.36	6.8	65.8	27.4
SB12	0.37	17.4	52.7	29.9
SB43	0.38	26.5	45.4	28.1
KB42	0.38	0.0	91.3	8.7
CS1	0.38	0.0	85.8	14.2
SB13	0.39	25.4	43.3	31.3
CS7	0.42	7.6	53.0	39.4
SB23	0.43	33.9	29.7	36.4
SB33	0.44	63.0	8.6	28.5
TS12	0.46	0.0	68.6	31.4
TS11	0.47	4.9	56.9	38.3
CS6	0.48	28.8	25.7	45.5
TS42	0.48	10.5	56.8	32.7
CS3	0.49	10.3	54.5	35.3
TS22	0.50	0.0	80.2	19.8
SB73	0.52	33.3	18.1	48.6
CS12	0.53	15.1	38.6	46.3
KB13	0.53	15.1	38.6	46.3
CS9	0.55	0.0	58.4	41.6
KB43	0.55	9.8	44.3	45.9
SB22	0.58	4.4	45.6	50.0
KB12	0.60	24.2	29.5	46.3
CS4	0.63	9.9	32.3	57.8
SB11	0.65	4.2	38.6	57.2
CS10	0.66	25.9	15.3	58.8
TS32	0.76	0.0	43.1	56.9
KB21	0.77	31.7	0.0	68.3
KB41	0.78	22.0	4.9	73.0
TS21	0.82	0.0	23.2	76.8
KB11	0.83	31.6	0.0	68.4
KB33	0.84	21.1	0.0	78.9
CS11	0.88	32.7	5.3	62.0
TS31	1.00	11.4	1.0	87.6
KB32	1.02	27.8	0.0	72.2
CS2	1.11	33.4	0.0	66.6
TS51	1.16	0.0	11.2	88.8
KB31	1.17	32.6	0.0	67.4

Figure S-1. Map showing positions of the surface sediment sampling stations in four study areas and diagrams of mean summed concentrations (µg.kg-1 dry weight) for three groups of PAHs: parent unsubstituted (red bar), alkyl-substituted (black bar) and polycyclic aromatic sulphur heterocyclic compounds (yellow bar; summed unsubstituted and alkyl-substituted).

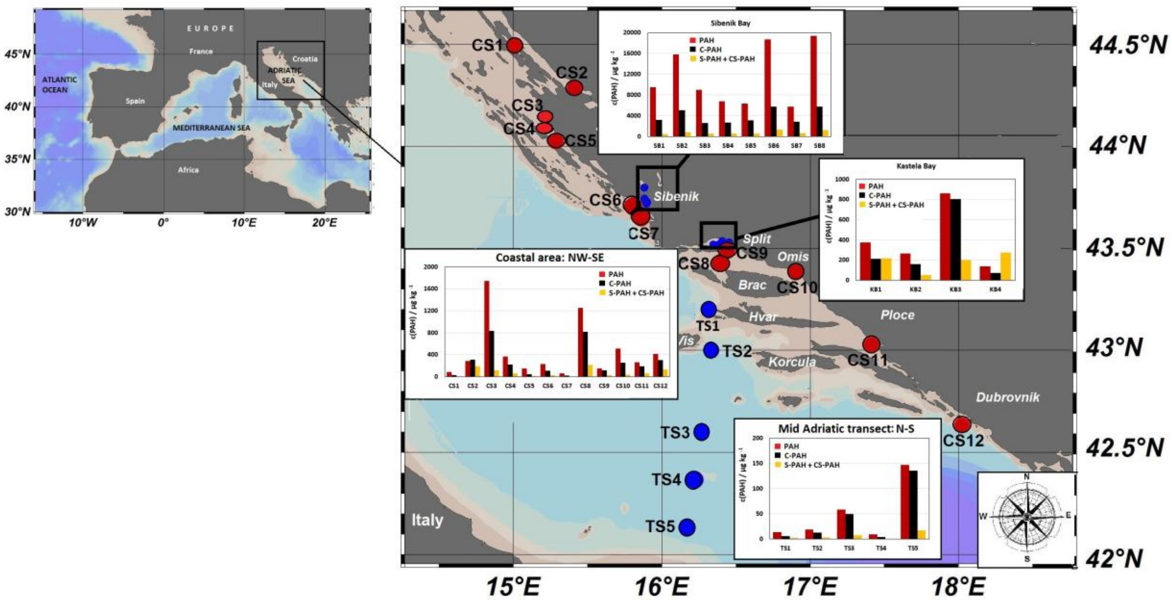

Figure S-2. Correlations between unsubstituted ΣPAH and their alkyl substituted homologues ΣC-PAH in the sediments from Šibenik Bay (SB. squares and stars; right ordinate). Kaštela Bay (KB). Costal survey (CS.) and mid-Adriatic transect (TS.) all triangles (left ordinate). COM 1 and 2 (diamonds) pyrogenic and PETRO petrogenic (diamonds) points from model source profiles from receptor environment computation by alternative least square ALS.

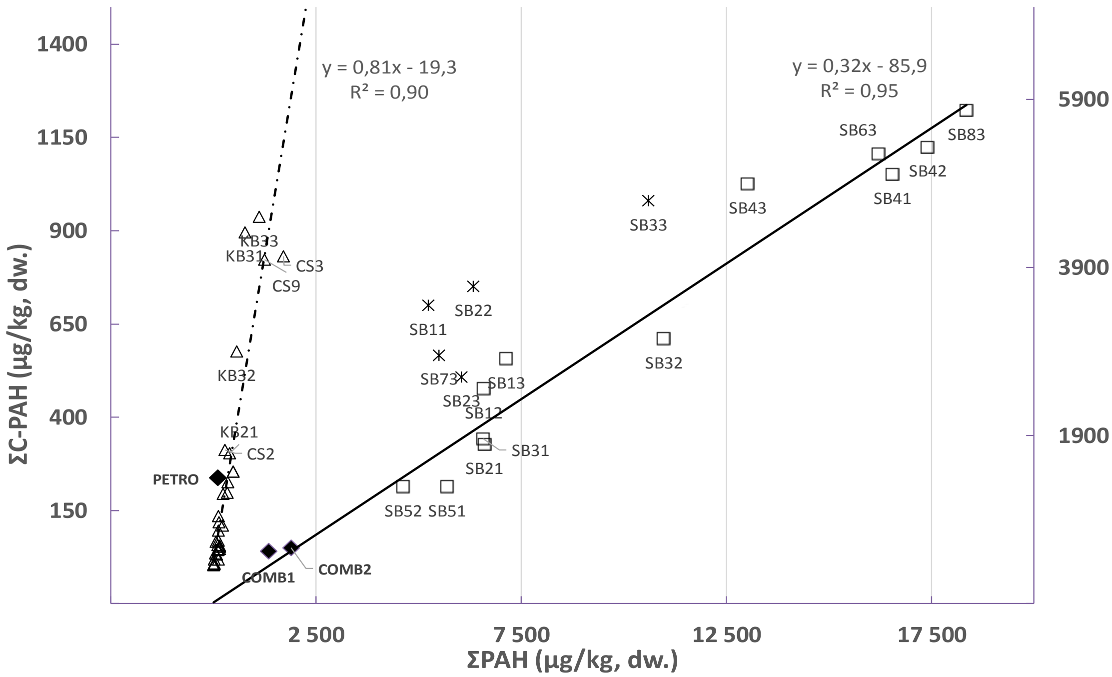

Figure S-3. Principal component analysis (PCA) sample scores accounting for maximal amount of variation (A) and a hierarchical cluster analysis (HCA) dendrogram with stations grouped according to Euclidean distance set on a similarity scale at 0.8 – dotted vertical line (1 indicates identical samples; B); computation done on pre-processed auto-scaled data with PCA varimax normalized rotation for two principal components and the HCA incremental linkage method.

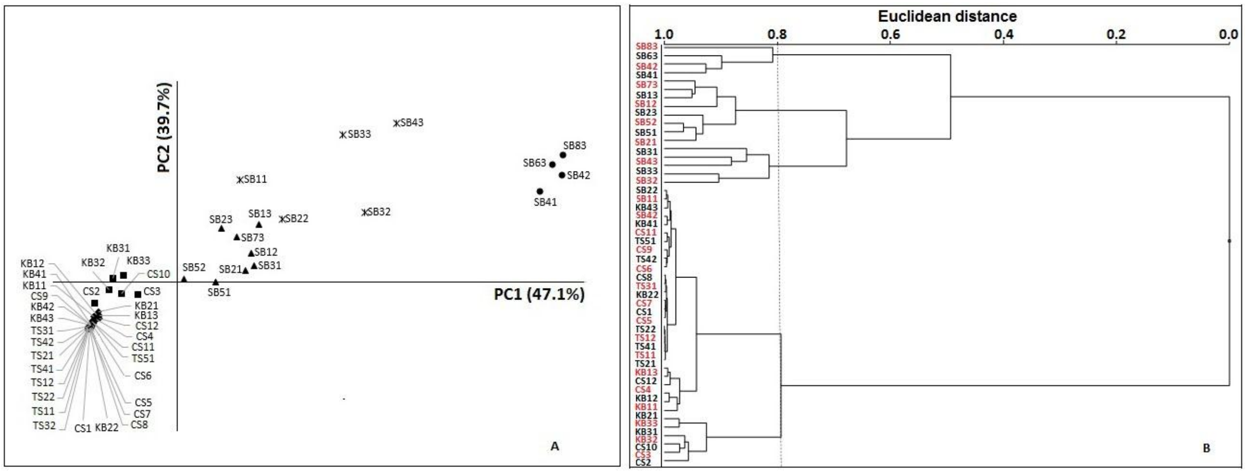

Figure S-4. Relative contributions (%) of two pyrogenic and one petrogenic sources of PAH in the sediments at each investigated station; data arranged in the order from the lowest to the highest petroleum contribution. This presentation indicates that two source model mixture may well describe PAHs composition.

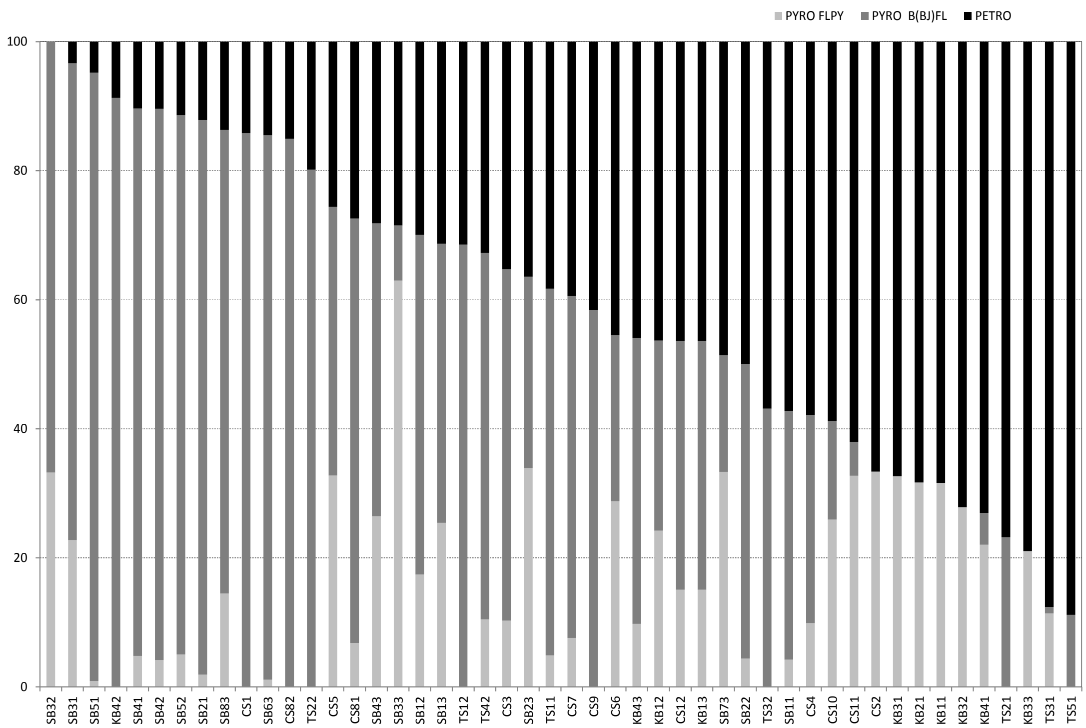

Figure S-5. Correlation of Alkyl/Parent PAH ratio (∑C-PAH/∑PAH) with petrogenic source contribution based on ALS receptor model calculation. This presentation indicates that Alkyl/Parent PAH ratio may be an excellent proxy for estimation of petrogenic source contribution.